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Canaigre Investigations†

VI. Extraction with Organic Solvent-Water Solutions*

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In a previous paper[5], it was reported that extraction of canaigre with a 50 per cent acetone–water solution gives tannin values ranging from 27.6 to 38.2 per cent as compared with 22.0 to 31.7 per cent obtained by water extraction. The effects of concentration of acetone, time of extraction and volume of extractives were studied at 60° C. Canaigre tannin was easily soluble under the conditions studied.

Grassmann and Kuntara[4] reported that in the extraction of pine, larch and oak barks with methanol, ethanol and acetone, the yields of tannin were considerably higher than with the conventional water extractions. Stather, Lauffmann and Bau Miau[7] have proposed a method of identifying tannins from different sources by their different solubilities in solvents, such as, methanol, ethanol and acetone, and mixtures of these with water.

The high yields and improved quality obtained by organic solvent–water extraction of canaigre for analysis have stimulated interest in the possible commercial utilization of the process. Such a development would require the successful solution of major engineering and financial problems. Equipment would have to be designed to prevent leakage of the volatile solvents, both for safety and for economy. Efficient and inexpensive recovery of solvent, both from the liquors and from the spent canaigre, would be necessary. These problems, however, are not dealt with here; the present study was designed merely to determine whether solvent–water extraction is sufficiently superior to water extraction to justify the research necessary to establish a feasible commercial process.

The tannin values on all fresh and spent canaigre samples used in the tests reported in this paper were obtained by a method which has given accurate and concordant results[5] in this laboratory. This method consists in extracting with 500 ml. of a 50 per cent acetone–water solution at 60° C. sufficient of the finely ground material to give 4 grams of tannin per liter. The acetone is distilled from the collected liquor, and the water solution made to a volume of 1 liter. The liquors thus obtained and all other liquors obtained in the extraction studies were analyzed by the Official methods of the American Leather Chemists Association[1].

*This is the sixth of a series of papers reporting various phases of cooperative investigations of canaigre as a source of tannin by the Bureau of Agricultural and Industrial Chemistry and the Bureau of Plant Industry, Soils and Agricultural Engineering, Agricultural Research Administration, United States Department of Agriculture.

**One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, United States Department of Agriculture.

†Presented at the Forty-Fifth Annual Meeting of the American Leather Chemists Association, Spring Lake, N. J., June 23, 1949.

Preliminary Tests to Determine Effects of Temperature, Time, Concentration, and Nature of Solvent

Tannin solutions for analysis are not suitable for commercial use because of their low tannin concentration, but several preliminary tests were made at this low tannin concentration because of the greater ease of manipulation. In the first test, seven samples of canaigre from Texas and two from Arizona were ground in a Wiley mill to pass a 1 mm. screen. The method of extraction used was essentially the same as that described in the preceding paragraph except that the temperatures and acetone concentrations were varied. Extractions were made at 23°, 30°, 40°, 50°, and 60° C. At each of these temperatures, acetone–water solutions of 10, 25 and 50 per cent acetone were added at regular intervals and allowed to percolate through the sample. The liquor removed, 500 ml. in 5 hours, was freed of acetone by distillation, and analyzed.

The data in Table I show that the average values for tannin and purity for each concentration of acetone are fairly constant at temperatures from 23° to 60° C. The amount of tannin removed by 25 or 50 per cent acetone is greater than that removed by a 10 per cent concentration. During the tests a definite clogging of the extractor occurred with acetone concentrations of 10 and 25 per cent at 60° C. These results confirm previous published data on extraction above 50° C. with acetone concentrations of 25 per cent or less. Constant tannin values were obtained at all the extraction temperatures studied with the 25 and 50 per cent acetone–water mixtures, and no mechanical difficulty was experienced with the 50 per cent concentration at any temperature studied.

TABLE I

Effects of Temperature and Concentration of Solvent on Extraction of Canaigre* with Acetone-Water Solutions

(Moisture-Free Basis)

	Acetone Per Cent	Extracted at 23° C.	30° C.	40° C.	50° C.	60° C.
		Per Cent	Per Cent	Per Cent	Per Cent	Per Cent
Tannin†	10	30.0	30.2	30.2	30.6	28.5
	25	31.8	32.0	32.0	31.9	31.7
	50	31.8	32.1	31.9	32.0	32.0
Purity † ‡	10	58.7	58.7	59.0	59.2	58.5
	25	59.8	60.7	60.6	60.5	60.4
	50	60.5	60.8	60.7	60.5	60.3

* Extracted in a Reed-Churchill extractor.
† Average values for tannin and purity for all 9 samples.
‡ Purity is 100 times the value for tannin divided by that for soluble extractives.

A second test was made in which the canaigre was extracted by a batch washing process instead of the percolation process used in the first test. Extraction temperatures were 23°, 40° and 60° C. The stirring periods were

10, 20 and 30 minutes. The acetone–water mixtures contained 10, 25 and 50 per cent of acetone. For each of the tests, the quantity of canaigre needed to give 4 grams of tannin was weighed into a 400 ml. beaker. The acetone–water solution was added in the ratio of 1 liter of solution to 100 grams of sample, and the mixture was stirred slowly for the specified time at the designated temperature. The liquid was separated from the solids by means of a laboratory-type basket centrifuge. The solid matter on the centrifuge screen was washed once with the same volume of the same acetone–water solution

TABLE II

Effects of Temperature, Time and Concentration on Batch Extraction of Finely Ground Canaigre* with Acetone-Water Solutions

(Moisture-Free Basis)

Acetone	Stirring Time	Total Extractives	Soluble Extractives	Insolubles	Non Tannin	Tannin	Average Tannin	Purity†	Tannin Recovery‡
Per Cent	Minutes	Per Cent	Per Cent	Per Cent	Per Cent	Per Cent	Per Cent	Per Cent	Per Cent
				Extracted at 23°C.					
10	10	50.5	48.9	1.6	20.4	28.5		58.3	
10	20	49.7	48.1	1.6	20.2	27.9	28.1	58.0	82.4
10	30	49.7	48.3	1.4	20.3	28.0		58.0	
25	10	53.1	51.5	1.6	20.2	31.3		60.8	
25	20	54.6	52.7	1.9	20.6	32.1	31.5	60.9	92.4
25	30	53.9	52.3	1.6	21.1	31.2		59.7	
50	10	52.9	51.7	1.2	20.2	31.5		60.9	
50	20	52.7	51.7	1.0	19.8	31.9	31.7	61.7	93.0
50	30	53.5	51.9	1.6	20.1	31.8		61.3	
				Extracted at 40°C.					
10	10	52.2	51.0	1.2	20.7	30.3		59 4	
10	20	51.4	49.9	1.5	20.5	29.4	29.8	58.9	87.4
10	30	51.9	50.2	1.7	20.6	29.6		59.0	
25	10	55.0	51.7	3.3	20.5	31.2		60.3	
25	20	55.7	52.4	3.3	20.9	31.5	31.1	60.1	91.2
25	30	53.1	51.0	2.1	20.4	30.6		60.0	
50	10	55.1	52.0	3.1	20.3	31.7		61.0	
50	20	54.2	53.0	1.2	20.4	32.6	32.3	61.5	94.7
50	30	54.5	53.0	1.5	20.4	32.6		61.5	
				Extracted at 60°C.					
10	10	52.2	48.4	3.8	20.2	28.2		58.3	82.7
10	20	43.0	40.0	3.0	18.4	21.6		54.0	63.3
10	30	43.9	41.1	2.8	19.2	21.9		53.3	64.2
25	10	53.9	52.6	1.3	20.3	32.3		61.4	94.7
25	20	51.6	49.3	2.3	20.0	29.3		59.4	85.9
25	30	48.1	45.5	2.6	19.3	26.2		57.6	76.8
50	10	54.5	52.9	1.6	20.1	32.8		62.0	
50	20	54.1	52.4	1.7	20.0	32.4	32.6	61.8	95.6
50	30	54.6	53.2	1.4	20.5	32.7		61.5	

* Filtered by a small laboratory-type centrifuge.

† Purity is 100 times the value for tannin divided by that for soluble extractives.

‡ Based on a value of 34.1 per cent tannin obtained by extraction in a Reed-Churchill extractor with a 50 per cent acetone-water solution.

and at the same temperature as used originally, with the centrifuge running at full speed. The liquors were combined for analysis.

The data in Table II show that, in general, the highest values for recovered tannin were obtained with the 50 per cent acetone–water solution at all temperatures studied. Prolonged stirring had little effect on the amount of tannin removed. The 10 per cent acetone–water solution gave the lowest tannin recovery, and at 60° C., because of the gelatinization of starch, difficulty was encountered in separating the extractives. Prolonged stirring at this temperature decreased the efficiency of extraction.

The extraction with 25 per cent acetone–water solutions gave results in agreement with those obtained with 50 per cent. When stirred for more than 10 minutes at 60° C., however, a definite decrease in recovered tannin resulted, indicating gelatinization of starch.

The data indicate that finely ground canaigre can be easily extracted at a low temperature (23° to 40° C.) with either 25 or 50 per cent acetone–water solutions. The 10 per cent acetone–water solution does not give efficient extraction at 23° C., and at 60° C. there is a marked decrease in recovered tannin because of gelatinization of starch.

A third preliminary test was made to compare solvents. The batch system described for the second test was used. Canaigre was extracted at 60° C. with 50 per cent solutions of methyl alcohol, ethyl alcohol and acetone, respectively, in water. The time of stirring was 30 minutes and the liquid was separated from the solid both with a centrifuge and with a Büchner funnel.

TABLE III

Effects of Different Solvents in Extraction of Finely Ground Canaigre

(Moisture-Free Basis)

Type of Extraction	Solvent	Total Extractives	Soluble Extractives	Insolubles	Non Tannin	Tannin	Purity†	Tannin Recovery
		Per Cent	Per Cent	Per Cent	Per Cent	Per Cent	Per Cent	Per Cent
Centrifuge*	Methyl Alcohol	54.4	52.1	2.3	17.7	34.4	66.0	90.0
Centrifuge*	Ethyl Alcohol	55.2	51.8	3.4	16.9	34.9	67.4	91.4
Centrifuge*	Acetone	57.4	53.5	3.9	17.3	36.2	67.7	94.8
Büchner Funnel*	Methyl Alcohol	52.6	52.0	0.6	17.3	34.7	66.7	90.8
Büchner Funnel*	Ethyl Alcohol	55.9	53.3	2.6	17.5	35.8	67.3	93.7
Büchner Funnel*	Acetone	56.2	53.9	2.3	17.4	36.5	67.7	95.6
Reed-Churchill‡	Acetone	59.5	56.3	3.2	18.1	38.2	67.8	100.0

* Extracted with 50 per cent solvent-water solutions for 30 minutes at 60° C.

† Purity is 100 times value for the tannin divided by that for soluble extractives.

‡ Extracted by percolation to 500 ml. in 5 hours (analytical method).

The data (Table III) indicate that any of the solvent–water solutions give tannin recovery of 90 per cent or more under the conditions used. The acetone-water solution is more efficient than the other solvent-water solutions, giving approximately 2 to 5 per cent more tannin recovery than the alcohols. Ethyl alchol is slightly superior to methyl alcohol. The superiority of the Büchner funnel to the centrifuge is undoubtedly due to a more complete liquid-solid separation.

Countercurrent Extraction with Organic Solvent–Water Solutions

The preliminary tests described above indicated the most suitable conditions for the extraction of canaigre. Tests were then made with quantities of canaigre large enough to give liquors of tannin strength comparable to that which would be obtained in commercial practice.

Practical experience over many years and work in this laboratory have shown that canaigre tannin cannot be successfully extracted with water by the conventional leaching methods used with usual tanning materials in stationary leaches. The factors involved in these methods are the solubility of tannin in water, the permeability of water into the particles of the tanning material, the diffusion of the tannin through the cell walls and the pores of the tanning material, and the percolation of the water or liquor through the solid material. The first of these involves no problem, as tannin is completely and readily soluble in water. To insure the highest rate of permeability and diffusion, fine comminution is required. The obvious explanation is that in fine grinding the exposed surfaces are greatly increased and a large proportion of the cell walls are ruptured. However, fine comminution hinders and may even prevent the percolation of water or liquor through the solid material. In commercial practice, therefore, extraction is a compromise between these two factors. The material is ground to as fine a condition as will still permit percolation. Permeability and diffusion are then increased by raising the temperature to as near boiling as the nature of the material will permit.

The extraction of canaigre presents special problems. The starch slows percolation and diffusion and does not permit high temperatures, which cause it to swell and clog the system. In large-scale extraction of canaigre, percolation has been easily obtained by the use of large particles and low temperatures, but the yield of tannin has been poor. Beebe, Cordon and Rogers [2], [3] have proposed a method by which the tannin can be efficiently removed. By this method the finely comminuted, but not necessarily powdered, material is thoroughly stirred with water at 40° to 46° C. The liquor is subsequently separated from the solid material with a centrifuge or other equipment that gives efficient separation of liquids from solids. This method forms the basis for the procedure used in the following extraction tests.

In the first test, the method consisted of grinding canaigre to pass a 1 mm. screen. One hundred gram portions of the air-dry material were weighed

TABLE IV

Countercurrent Extraction of Finely Ground Canaigre With a 25 Per Cent Acetone-Water Solution

Head Liquor No.	Original Volume	After Removal of Solvent		Analysis of Solution After Removal of Solvent					Tannin Recovery	Extraction Efficiency*	Total Tannin Accounted for**
		Volume	Barkometer	Soluble Extractives	Insolubles	Non Tannin	Tannin	Purity			
	Ml.	Ml.	Degrees	Per Cent	Per Cent	Per Cent	Per Cent	Per Cent	Grams	Per Cent	Per Cent
1	420	248	65.0	14.4	0.9	5.1	9.3	64.3	23.0		
2	450	282	64.0	14.1	0.9	5.3	8.8	62.1	24.6		
3	400	230	70.0	15.6	1.2	6.1	9.5	61.2	22.0		
4	540	356	14.3	3.3	0.3	1.2	2.1	64.0	7.4		
5	400	250	9.0	1.0	0.3	0.3	0.7	70.0	1.8		
6	515	349	2.5	0.7	0.2	0.2	0.5	77.4	1.9		
7	455	295	0.7	0.6	0.2	0.1	0.5	82.2	1.4		
Total	3180	2010							82.1	90.8	95.0

*Percentage of tannin recovered based on that in original material (33.8 per cent or 90.4 grams)

**Percentage of tannin in liquors and spent material based on that in original material. (The spent material contained 3.1 per cent or 3.8 grams of tannin.)

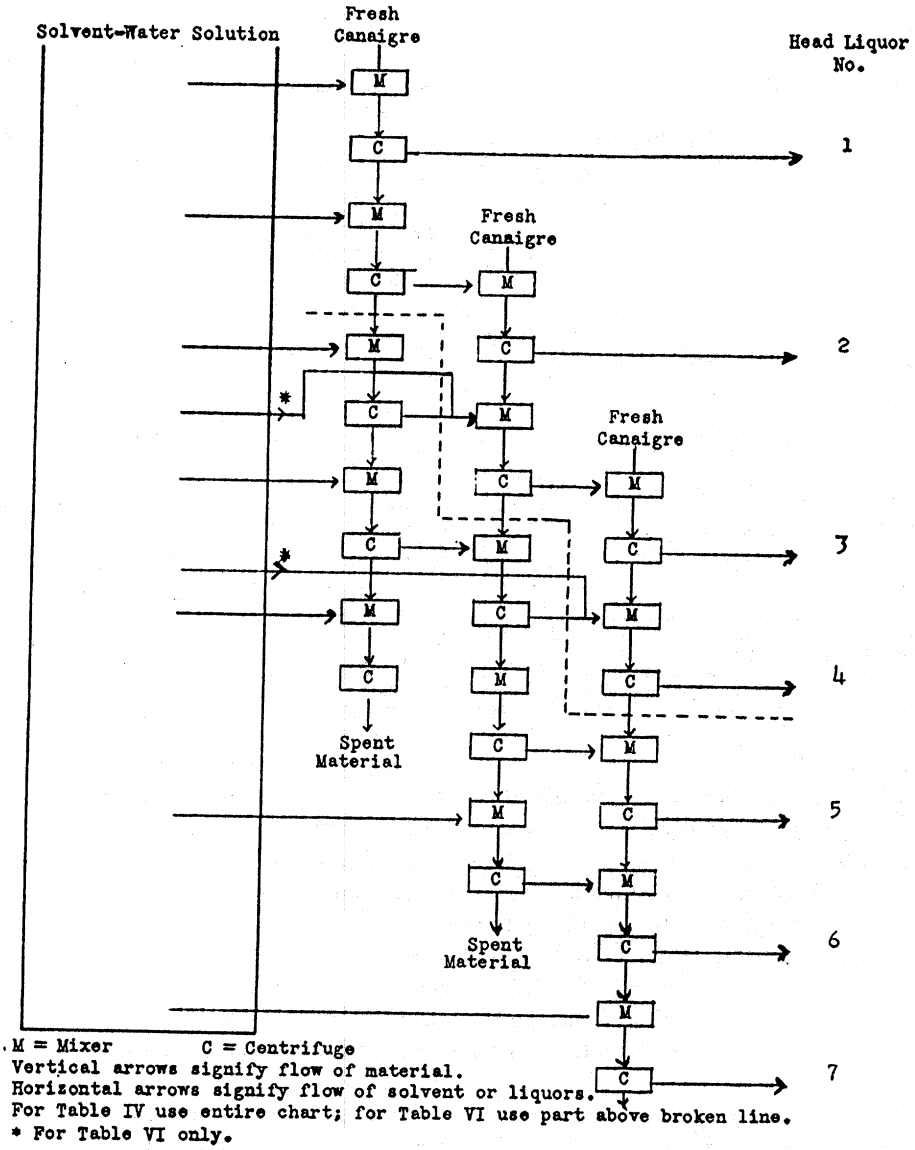

FIGURE 1.—Flow Sheet of Countercurrent Extraction System Used to Obtain Data in Tables IV and VI.

into beakers, and 500 ml. of a 25 per cent acetone-water solution was added. The mixtures were stirred moderately at room temperatures for 15 minutes. The liquors were then centrifuged from the solid matter, and prepared for analysis as before. The complete records of weights, volumes, barkometer strengths, and tannin contents provided means of calculating extraction

TABLE V

Extraction of Canaigre with 25 Per Cent Acetone-Water Solutions

*Summarized Data From Four Tests**

Original Material	*Test 1*	*Test 2*	*Test 3*	*Test 4*
Tannin—Per Cent	33.8	33.8	32.3	20.2
Tannin—Grams	90.4	92.8	445.3	325.2
Purity—Tannin x 100/Soluble Solids	65.6	65.6	63.4	49.2
Liquor Removed				
Tannin—Grams	82.1	85.7	413.2	298.2
Purity—Tannin x 100/Soluble Solids	63.2	63.7	63.4	49.7
Spent Material				
Tannin—Per Cent	3.1	3.0	2.5	3.1
Tannin—Grams	3.8	3.8	—	—
Purity—Tannin x 100/Soluble Solids	65.7	55.8	60.4	62.4
Extraction Efficiency—Per Cent	90.8	92.4	92.8	91.7
Total Tannin Accounted for—Per Cent	95.0	96.4	—	—

* Test 1 shows summarized data from Table IV.

Test 2 gives data from a test on the same sample used in Test 1, but here a solution to canaigre ratio of 750 ml. to 100 grams.

Tests 3 and 4 give summarized data obtained with two different strains of canaigre extracted on a somewhat larger scale; three washes with solvent-water solutions at 45°C. were used.

All extractions made by mixing and centrifuging in a countercurrent system.

efficiency. Table IV shows the data, and Figure 1 shows a flow sheet of the method used. They indicate that tannin removal is rapid and that three-quarters of the tannin is removed with one extraction. An extraction efficiency of 90.8 per cent was obtained, and only 3.1 per cent tannin was left in the spent material. Another test was made by the same method, except that the ratio was 750 ml. solution to 100 grams of canaigre. Two further tests were made by a similar method with two different strains of canaigre. These were made on a somewhat larger scale at 45° C.; a system with three washes was used. Table V shows the results of these tests, together with a summary of the results in Table IV. The extraction efficiencies here range from 90.8 to 92.8 per cent.

Comparative extractive studies were made in which extraction solutions were 25 per cent methyl alcohol, ethyl alcohol, isopropyl alcohol*, and acetone in water. In these tests, the solvent to canaigre ratio was 750 ml. to 100 grams. Only two extractions were made on each batch of canaigre. The portion of the flow sheet in Figure 1 above the dotted line indicates the method used. The first batch of canaigre was given two extractions in succession with fresh solution; the other two batches were extracted first with liquor from the second extraction of the previous batch, and then with fresh solution. Table VI shows the data. Of the solvent solutions studied, acetone

*This solvent was suggested by the Chemical Engineering and Development Division of this Laboratory.

gave the best extraction efficiency, followed by isopropyl alcohol, ethyl alcohol and methyl alcohol. These results are confirmed by analyses of the spent material, which increased from 4.5 per cent tannin in the acetone-extracted material to 12.7 per cent in the spent material from methyl alcohol.

TABLE VI

Countercurrent Extraction of Finely Ground Canaigre with 25 Per Cent Solvent-Water Solutions

Description	Weight*	Barkometer	Tannin	Content	Purity	Tannin† Accounted for	Extraction‡ Efficiency
	Grams	Degrees	Per Cent	Grams	Per Cent	Per Cent	Per Cent
25 Per Cent Alcohol Solution							
Original Material	271.1		33.8	91.6	65.6		
Head Liquor 1	425	31.7	4.7	20.0	60.0		
2	348	49.0	6.5	22.6	60.4		
3	462	35.5	5.0	23.1	60.6		
4	556	3.0	0.9	5.0	71.5		
Total Liquors				70.7			77.2
Spent Material	150.4		12.7	19.1	79.6		
Liquors and Spent Material				89.8		98.0	
25 Per Cent Ethyl Alcohol Solution							
Original Material	274.2		33.8	92.6	65.6		
Head Liquor 1	452	36.0	5.0	22.6	62.4		
2	401	44.0	6.1	24.5	62.3		
3	484	39.5	5.5	26.6	62.8		
4	467	2.5	0.9	4.2	69.8		
Total Liquors				77.9			84.1
Spent Material	140.5			11.7	70.8		
Liquors and Spent Material				89.6		96.8	
25 Per Cent Isopropyl Alcohol Solution							
Original Material	270.8		33.8	91.5	65.6		
Head Liquor 1	505	33.2	4.5	22.7	63.4		
2	482	38.7	5.5	26.5	63.7		
3	460	39.5	5.5	25.3	62.8		
4	563	4.2	0.8	4.5	69.8		
Total Liquors				79.0			86.3
Spent Material	133.8			8.6	71.1		
Liquors and Spent Material				87.6		95.7	
25 Per Cent Acetone Solution							
Original Material	274.3		33.8	92.6	65.6		
Head Liquor 1	422	41.5	5.9	24.9	65.2		
2	424	42.8	5.8	24.6	61.9		
3	480	44.3	6.2	29.7	64.5		
4	530	5.7	1.0	5.3	74.6		
Total Liquors				84.5			91.3
Spent Material	134.3			6.0	65.3		
Liquors and Spent Material				90.5		97.7	

* Weight of liquors after distillation of solvent; weight of solid material on moisture-free basis.
† Percentage of tannin in liquors and spent material based on that in the original liquor.
‡ Percentage of tannin in recovered liquors based on that in the original material.

The data show that under the extraction condition used, the 25 per cent acetone-water solutions gave the best results in the extraction of finely ground canaigre. One advantage of acetone over ethyl or isopropyl alcohol is that complete removal of the organic solvent by distillation is much easier. Another advantage is that the liquors from the acetone-water extraction are much clearer after distillation than those from the water-alcohol extractions (Table VII). All organic solvents dissolve some material insoluble in water. In acetone-water extracted liquors, this material settles rapidly and completely after distillation of the acetone and is easily removed.

TABLE VII

Analyses of Fermented Canaigre Liquors Prepared by Extraction with Solvent-Water Solutions

Experiment No.	Extraction	Liquor	Soluble Extractives	Insolubles	Non Tannin	Tannin	Purity	Total Sugar
			Per Cent	Per Cent	Per Cent	Per Cent	Per Cent	Per Cent
1	25 Per Cent Acetone-Water	Control	9.3	0.7	3.4	5.9	63.3	2.0
		Control after settling†	9.1	0.0	3.4	5.7	62.3	—
		Fermented	7.4	0.4	2.1	5.3	70.7	0.6
2	25 Per Cent Acetone-Water	Control	6.4	0.3	2.3	4.1	63.7	—
		Control after settling†	6.2	0.0	2.3	3.9	62.6	1.2
		Fermented	4.7	0.3	1.1	3.6	76.9	0.3
3	17.5 Per Cent Isopropyl Alcohol Water	Control—Centrifuged‡	3.3	0.1	1.3	2.0	60.6*	0.7
		Fermented	3.0	0.1	1.0	2.0	66.1	0.4
4	25 Per Cent Isopropyl Alcohol Water	Control	8.3	0.7	3.1	5.2	62.6	—
		Control after settling†	7.8	0.3	2.7	4.9	63.5	1.7
		Fermented	6.2	0.7	1.5	4.7	76.0	0.2

* The relatively low purity of this liquor is due to incomplete extraction of large shreds.
† Allowed to stand overnight and decanted.
‡ Run through a supercentrifuge.

Solvent-Water Extraction in Stationary Leaches

It might be assumed that with a more efficient solvent than water fine comminution would not be necessary and tannin would be satisfactorily extracted from coarse particles by conventional leaching systems. Preliminary tests indicated that this was not true, and a leaching test was made to determine this point more positively.

An eight-vat countercurrent leaching battery was set up in a Reed-Churchill apparatus regulated to maintain a constant temperature of 50° C. The usual Reed-Churchill extraction tubes were used for vats. A 50 gram portion of coarsely shredded canaigre roots was placed in each vat and leached with a 50 per cent acetone-water solution with a solution to canaigre ratio of 500 ml. to 100 grams. The liquors were passed ahead every hour, giving the canaigre in each vat 15 extractions with liquor or water, in accordance with standard requirements for an eight-vat countercurrent leaching system. After the completion of each of these leaching cycles, the spent canaigre was removed and replaced with fresh material. The process was continued until the canaigre in 14 vats had been leached. Because of the absence of packing and channeling, this laboratory test gave a greater tannin recovery than would be obtained in commercial practice.

The canaigre used contained 245.4 grams of tannin. Analyses of all the liquors removed showed that 188.3 grams were recovered. The leaching efficiency was thus 76.7 per cent as compared with 90 to 93 per cent obtained by extracting fine particles prepared from the same lot of canaigre.

In all extraction processes so far tried, the solvent-water solution was more efficient than water alone, but for leaching coarse particles, the tannin recovery was still insufficient.

Fermentation of Liquors to Increase Purity

In the solvent-water extraction of canagire, the purity of the liquors taken off when the system is in equilibrium is at least as high as that of the original material. Therefore, if a strain of roots is used which has a purity above 60, the purity of the extract produced would be above 60, which would be satisfactory for most tanning purposes. In such cases it would not be necessary to increase the purity by the fermentation process described by Cordon, Beebe and Rogers [3]. It was considered desirable, however, to determine whether this process can be applied to liqours extracted with solvent-water solutions. It might be used to produce an extract with purity of 70 to 80 for blending with other low purity extracts, to utilize strains of roots with rather low purity or to improve the keeping qualities of the extract by removal of sugars. It might be found that the fermentation products are valuable enough to warrant their production and recovery.

Fermentation tests were made on liquors prepared by acetone-water and isopropyl alcohol-water extractions only, as it was believed that the results of extraction with methyl and ethyl alcohol did not justify their consideration. After distillation of the solvent, the aqueous liquors were inoculated with a strain of *Aerobacter aerogenes* (culture WH [3]) and incubated at 30° C. with aeration at the rate of one-fifth volume of air per volume of liquor per minute.

Analyses of some unfermented and fermented liquors are given in Table VII. These data show that liquors prepared by solvent-water extraction

can be readily fermented. Purities of nearly 77 were obtained. In experiments 1 and 3, the sugar was not completely fermented, probably because the fermentation was stopped before it was complete. The purity of the liquors from the solvent-water extractions increased less than that of the liquors from water extraction. This was due to a greater removal of tannin by the solvent-water extraction, resulting in a lower sugar to tannin ratio. The only difficulty encountered in the fermentation of these liquors from solvent extraction was with the isopropyl alcohol liquors. Here aeration produced a persistent foam not broken down by usual anti-foaming agents, such as octadecanol in soybean oil. This might be a rather serious drawback in the commercial-scale fermentation of these liquors.

Solvent Extraction of Spent Material From Water-Extracted Canaigre

The preceding tests were made by replacing water with solvent-water solution throughout the extraction system. Tests were also made in which the solvent-water solution was used only on material already extracted to a reasonable level by water alone. The advantage of such a system would be a saving of solvent and the use of only one container for the solvent operation, with consequent savings in construction and operating costs. Obvious disadvantages would be extra handling of material and the evaporation of more liquor.

Table VIII shows the results of acetone-water extraction of spent material. Tests 1 to 4 were made on typical spent material from water extraction. Tests 5 to 7 were made on material intentionally poorly extracted with water to determine whether solvent extraction of the spent material could compensate for poor results in the water extraction.

TABLE VIII

Acetone-Water Extraction of Canaigre after Water Extraction

Experiment No.	Type of Material Used	Tannin Recovery from Water Extraction*	Tannin in Water-Spent Material		Liquors from Solvent-Water Extraction			Tannin Recovery from Solvent-Water Extraction†	Over-all Extraction Efficiency‡
					Tannin		Purity		
		Per Cent	Per Cent	Grams	Per Cent	Grams	Per Cent	Per Cent	Per Cent
1	Fully spent	78.1	8.3	67.5	1.9	47.9	88.6	71.0	94.2
2	Fully spent	82.5	7.5	3.4	0.5	2.7	84.4	79.4	89.0
3	Fully spent	80.2	7.8	3.9	0.6	2.9	85.1	74.4	91.0
4	Fully spent	82.8	7.2	2.9	0.5	2.4	85.5	82.8	88.8
5	Partly spent	66.1	23.9	10.9	1.1	7.5	78.3	69.0	89.5
6	Partly spent	70.3	21.2	9.9	1.4	6.9	87.8	69.7	90.9
7	Partly spent	65.1	25.0	12.0	1.4	8.2	90.3	68.2	89.3

* Percentage of tannin in liquors from water extraction based on that in original material.

† Percentage of tannin in liquors from solvent-water extraction based on that in spent material after water extraction.

‡ Percentage of tannin in liquors from water extraction plus that in liquors from solvent-water extraction based on that in original material.

In this series of tests, the material was mixed and pressed in the same manner as in previous tests. In the first test, a batch of spent canaigre was divided into six portions. To the first portion was added the solvent-water solution in the ratio of 10 parts of liquid to 1 part of solid. After the material was mixed and pressed, the liquor was added to the second batch, and the operation was repeated until the liquor had been mixed with each of the six portions in succession. The liquor was then measured and analyzed. In the remaining tests, the water-spent material was extracted with only one portion of solvent-water mixture.

The solvent-water extraction of the normal water-spent material was slightly less efficient than total extraction with the solvent-water solution. It is possible that the lower cost of this method would compensate for the lower efficiency. Another method of lowering the total cost is suggested by tests 5 to 7, in which a less complete water extraction was used, as compared with thorough water extraction in tests 1 to 4.

Discussion

Since tannin is soluble in all proportions in water and only to a limited extent in the pure organic solvents [7] used, the reason for the increased tannin extraction from canaigre roots when solutions of these solvents in water are used is not readily apparent. Undoubtedly their inhibitive effect on the swelling and gelatinization of starch is an important factor. This is demonstrated by the fact that in extraction to prepare solutions of the low strength required for analysis, acetone-water mixtures percolate readily and dissolve the tannin completely at a moderate temperature, whereas water does not percolate through the powder, because of swelling and partial gelatinization of the starch. This phenomenon may be operative to some extent even at room temperature. Another factor which undoubtedly plays an important role is the action of solvents on compounds of tannin and protein. Canaigre roots contain considerable amounts of protein which react with the tannin on liberation by comminution. Merrill, *et al* [6] suggest that the solvents in water greatly facilitate the decomposition of the tannin-collagen compound by so altering the dissolved tannin that it is less reactive toward collagen. It is probable also that solvents similarly affect compounds of starch and tannin. That such factors are operative is indicated by the following experiment.

The liquor from properly harvested and dried canaigre settles rapidly. However, if canaigre is harvested during the growing season, the liquor contains much finely suspended material. Some of this material was filtered and washed with considerable difficulty. The moisture-free material contained roughly 40 per cent protein, 28 per cent starch and 7 per cent mineral matter. This material was then suspended in water, and a large volume of alcohol was added. The suspended matter was decomposed, and there was a rapid settling of a coarse precipitate, accompanied by a liberation of tannin into the solution. Analysis of this solution showed a content of approximately 10 per

cent tannin on the basis of the original moisture-free sediment. Acetone had the same effect as alcohol.

In our tests, acetone was the most efficient solvent. It should be apparent, however, that changes in conditions might alter this or that some solvent with a lower efficiency might in the long run be more economical. In the choice of solvents, all factors must be considered. As any solvent without efficient recovery would be prohibitively expensive, it follows that the cost of the solvent is determined mainly by the efficiency and cost of recovery and not by the intial cost. While a less volatile solvent might seem to involve less risk, any solvent used must be sufficiently volatile to be recovered economically and efficiently both from the recovered liquors and from the spent material, and therefore precautions would have to be taken for any solvent. It is also necessary to determine whether a solvent will dissolve from the canaigre material insoluble in water, which would be detrimental to the tanning extract produced, or if such material is dissolved, whether it could be easily removed.

Summary and Conclusions

Extraction of tannin from canaigre by solutions of water and some organic solvents was compared with extraction by water alone. Extraction of canaigre by an acetone-water solution increases the tannin recovery by 10 to 15 per cent, as compared with water extraction. Efficient water extraction of properly prepared material, gives only 80 to 85 per cent tannin recovery, but solvent-water extraction gives 90 to 93 per cent recovery.

With sufficient concentration of solvent in water, extraction is efficient even at a comparatively low temperature. On the other hand, a considerably higher temperature than that used for water extraction may be used if desired.

Although solvent-water leaching of large canaigre particles is more efficient than leaching with water alone, the resultant tannin recovery is not appreciably greater than that obtained by water extraction of finely comminuted material. Therefore, the use of a solvent-water solution in the usual commercial leaching process would not appear to be practical.

Because solvent-water extraction gives a finished extract with purity practically the same as that of the original material, if suitable material is used, no further processing is necessary to insure suitable purity. However, fermentation of these liquors to increase purity is feasible. It may be used to produce a high-purity extract or one of desirable purity from low-purity strains of canaigre, or to produce valuable by-products. Acetone is more satisfactory than ethyl, methyl or isopropyl alchols. Solvent-water extraction of the spent material obtained from water extraction may be more economical than a complete solvent-water extraction.

These tests have demonstrated that solvent-water extraction is more efficient than water extraction. They have indicated the choice of solvents and some of the factors involved in satisfactory extraction. The results

indicate that the process is sufficiently promising to warrant studies of the design of equipment required for extraction and for solvent recovery, and calculations of costs.

Acknowledgments

The authors acknowledge with thanks the assistance of M. E. Happich and E. E. Leach in conducting the analytical work, and of W. F. Happich, Jr. in conducting the leaching work.

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Discussion

G. W. Stanbery: I won't criticize Mr. Luvisi for not having started this work eighty years ago when we had exploitation of canaigre growing wild.

This discussion shows that we do have a source of tannin we need very largely. It recognizes the obstacles in extraction, the fly in the ointment, which is the starch, and progress is being made toward solving those problems.

Are there any comments or questions?

L. Sheard: Can you add any further information to the statement made a year ago with reference to the cultivation of sufficient canaigre to test the production of an extract on a manufacturing scale.

F. P. Luvisi: Perhaps Mr. Rogers would like to add a word to this.

J. S. Rogers: The work on the development of canaigre is progessing, I think, in a satisfactory manner but not as rapidly as we would wish. We have under cultivation and will be harvesting this year approximately five acres of canaigre. We also have growing at the present time 13 acres that will be available for harvest next year. The roots that will be harvested this year come from a type of canaigre that we have designated as the New Mexico type, or yellow root type. This strain does not have as high a tannin content or purity as the strain that comes from Arizona.

The thirteen acres that will be available for harvest a year from this coming fall contain canaigre of the Arizona or red root type. This canaigre has average tannin content which is considerably higher than the New Mexico type and gives a product that is of better purity, so that we anticipate that the material that we have to harvest next year will undoubtedly be a higher quality material.